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RADIATION AND LASER POTENTIAL OF HOMO- AND HETERO-NUCLEAR RARE---ETC(U)
DEC 77 W C WALKER, Y TANAKA AFOSR-77-3137

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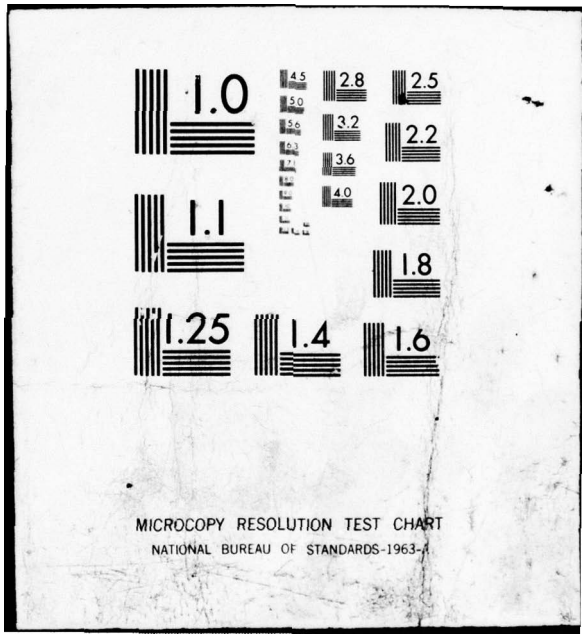
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(18) (19) REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER (6) AFOSR TR- 78 - 0175	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER (9)	
4. TITLE (and Subtitle) RADIATION AND LASER POTENTIAL OF HOMO- AND HETERO-NUCLEAR RARE-GAS DIATOMIC MOLECULES.	5. TYPE OF REPORT & PERIOD COVERED Annual Technical Rept. 1 Oct 76 - 1 Oct 77
	6. PERFORMING ORG. REPORT NUMBER (15)
7. AUTHOR(s) (10) William C. Walker, Yoshio Tanaka	8. CONTRACT OR GRANT NUMBER(s) AFOSR-77-3137
9. PERFORMING ORGANIZATION NAME AND ADDRESS (16) The Regents of the University of California, The Quantum Institute, University of California, Santa Barbara, California 93106	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (17) 2303 B1, 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR/NC, Bolling AFB, D.C. 20332	12. REPORT DATE (11) December 1, 1977 (1 Dec 77)
	13. NUMBER OF PAGES (12) 24 (15p)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Rare gas diatomic molecules
Vacuum ultraviolet spectroscopy
Excimers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Emission spectra from the vacuum ultraviolet to the visible region have been obtained from the rare gas dimers of helium, neon, argon and krypton and from the xenon oxide excimer. Several new discrete and diffuse bands together with both structured and unstructured continua have been observed and some have been tentatively identified with specific electronic states of the molecule. Several of these spectra appear only under specific excitation conditions and were thus revealed in this research for the first time. Significant new results for helium and argon dimers have been obtained

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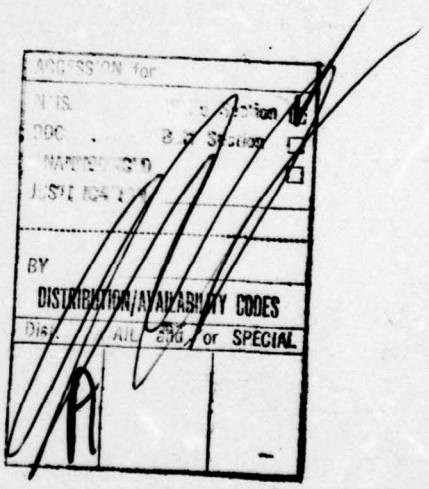
BOX 20

A study of the higher excited states of rare gas - oxide and sulfide excimer is underway.



AFOSR-TR- 78-0175

RADIATION AND LASER POTENTIAL OF HOMO- AND HETERO-NUCLEAR RARE-GAS DIATOMIC MOLECULES

Annual Technical Report

for

AFOSR Grant #77-3137

October 1, 1976 - October 1, 1977

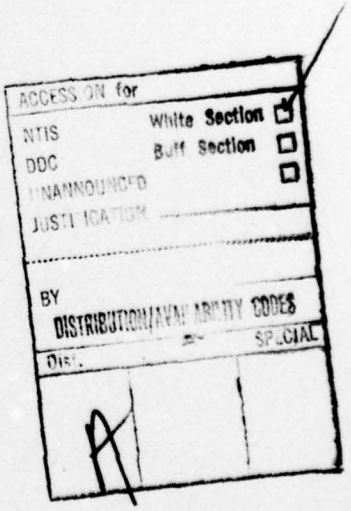
W.C. Walker
Principal Investigator

Y. Tanaka
Co-Principal Investigator

December 1, 1977

RESEARCH OBJECTIVES

This research involves a spectroscopic investigation of the electronic, vibrational and rotational levels of homo- and hetero-nuclear rare gas dimers and excimers of current interest for the development of middle and VUV lasers. The aim of the research is to obtain an unambiguous identification of the origin of the emission bands of rare gas dimers and rare gas halide and chalcogenide excimers and determine the energies of these excited states and derive accurate molecular constants and potential energy curves.



I. *STATUS OF THE RESEARCH*

The first three months of the current grant period (October 1, 1976 to December 30, 1976) were devoted to installing and aligning the VUV spectrographs and constructing appropriate light sources and gas handling systems. From January 1, 1977 on, we have been studying emission spectra from the dimers Ar_2, Ne_2 and He_2 in the 500-2000 Å region, principally with a 2 meter spectrograph. Emission spectra were taken under a variety of excitation conditions with both room temperature and liquid nitrogen cooled discharges. Excitation systems differing principally in current density and ratio of high to low frequency components were used to selectively excite high electronic states for study. Recently we have developed an efficient method for exciting rare gas oxide excimers utilizing an R.F. discharge in the megacycle frequency region. Since the data are not completely analyzed as yet, only a few of the most interesting results and interpretations are described below.

A. Argon Dimer: Ar_2

Dimer spectra in argon were excited principally in a Tesla coil discharge. Three series of band groups were observed and measured in the 1067-1222 Å region. One series appears between

1073-1125 Å. It consists of 17 band groups each of which consist of several sharp bands and associated dissociation continuum. This is the band series represented by the electronic transition $4s\ ^3\Sigma_u^+\ (1_u) \rightarrow 3p^6\ ^1\Sigma_g^+\ (0_g^+)$, the lower state being the ground state of Ar_2. This transition represents the band system I classified from absorption spectra.

A second band series occurs in the 1067-1222 Å region. It consisted of 22 band groups but none of the individual group was resolved into a number of discrete bands even in the spectrum taken with higher order of the high resolution spectrograph. We classified this series as due to transition $4s\ ^1\Sigma_u^+\ (0_u^+) \rightarrow 3p^6\ ^1\Sigma_g^+\ (0_g^+)$, which corresponds to the band system II of Ar_2 previously observed in absorption. The four well-resolved discrete bands observed in absorption in the 1068-1073 Å region of this band system are not observed in emission and instead this region is occupied by three diffuse structureless emission spectra. Serious inconsistencies observed between the emission and absorption spectra of this system can be reconciled by the suggestion that since this is a strong band system, individual emission bands will be easily absorbed by small amounts of argon dimer existing in its ground state in the discharge. The dissociation continuum, which appears in association with the individual band group, will not

easily be self absorbed and as a result we observe a series of short continua.

In the region between the two resonance lines of ArI at 1048 and 1066 Å, a number of emission bands and a large number of sharp absorption bands are observed simultaneously. We believe, in this stage of the work, that these all belong to band system III produced by transition $4s'\ 0_u^+ \leftrightarrow 3p^6\ {}^1\Sigma_g^+\ (0_g^+)$, again the lower state is the ground state. Since this band system is the strongest of the three, the absorption spectra dominate and this accounts for the observation of many sharp absorption and apparent emission bands.

In addition to the three band systems stated above, we also observed 15 emission bands which appeared in the 1110-1157 Å region. When argon was mixed with other rare gases such as helium or neon the bands appear slightly enhanced. The bands appear stronger when argon pressure is low, ~1 torr, and they are excited much more strongly by pulsed transformer discharge rather than by a Tesla coil discharge. The individual bands are quite diffuse yet show a degradation toward short wavelength. The origin of these is unknown at this time. By analogy with Mulliken's potential curves for Xe_2, these bands could be produced by transitions from one or more of the $5d\Pi\ (0_u^+,\ 1_u)$ states to the ground state. In addition to these band spectra, we also observe the well known emission continua

called "first continuum" with a peak at 1070 Å and "second continuum" with a peak at 1270 Å. By buffering argon with helium or neon we find that band system II vanishes simultaneously with the second continuum. Both may be restored by increasing the argon concentration. This strongly suggests that the second continuum arises from the same electronic transition responsible for band system II and that the peak of the second continuum is due to transitions from the lowest upper vibration level v'=0 to the purely repulsive part of the ground state potential. The origin of the first continuum is as yet unknown. The spectrum near the resonance line at 1066.6 Å within about ±9 Å is a mixture of a) broadened resonance line, b) a small part of band systems I and II and c) a true continuum. It is difficult, however, to find energy levels which will produce a pure continuum in this region in combination with the ground state.

B. Neon Dimer: Ne_2

The Ne_2 spectrum was studied under a variety of excitation conditions in the 600-1000 Å region. Band system I, which corresponds in electronic assignment to band system II of Ar_2, was observed in emission. Approximately seven band groups were identified in the 744-754 Å region. Each individual group consists of two or three sharp bands and associated dissociation

continua. These band groups are produced by the transition $3s\ ^1\Sigma_u^+\ (0_u^+) \rightarrow 2p^6\ ^1\Sigma_u^+\ (0_g^+)$. No band groups, which correspond to band system I of Ar_2, were observed in neon. An additional band group, which corresponds to Ar_2 band group observed in the 1110-1157 Å region, was observed in the region 759-775 Å. the suggestion made for the origin of the similar group in Ar_2 probably applies also to neon.

C. Helium Dimer: He_2

The He_2 spectrum is well known in the 500-1100 Å region, however, we have found that the character of the spectrum is highly dependent on the type of excitation. With low current, high frequency excitation from a Tesla coil the intensity ratio of the two known prominent peaks at 674 and 818 Å of the helium continuum is reversed from that normally observed so that in our work the 674 Å peak becomes the stronger. In addition, the two strong Hopfield bands at 648 and 662 Å do not appear but are replaced by three bands at 645, 651 and 659 Å. It is thus possible to study these new bands for the first time. These new bands appear to terminate on the ground state as do the Hopfield bands. Further study of these bands and others in neon and helium is continuing.

Analysis of the bulk of the above results is still underway but already a few important new results have been obtained.

One of these is a determination of the $^1\Sigma_u^+$ to $^3\Sigma_u^+$ state separation in Ar_2. A paper reporting this result is being written. In addition, a method of studying the helium bands at 645, 651 and 659 Å in He has been developed. These bands apparently originate on states different from those of the Hopfield bands. Further work on these bands is in progress.

D. Krypton Dimer: Kr_2

The emission spectrum of the krypton dimer in the VUV region is not well known except for two continua, one peaking at about 1236 Å (first continuum) and the other at 1500 Å (second continuum).

In this work Kr_2 is excited by a transformer or a Tesla coil discharge in the pressure range 1-300 torr. The following is a summary of our recent results in Kr_2.

1. With the Tesla coil discharge, a long train of wavy structure was observed for the first time. It consisted of about 19 broad peaks and occupies the region 1250-1405 Å. It is very similar to band system II of Ar_2 in the following respects: a) it has a diffuse appearance and no discrete bands were observed; b) its location with respect to the KrI resonance line, 1236 Å, and the second continuum, 1500 Å; c) the number of diffuse peaks (~19) observed; d) energy

separation of consecutive peaks. Because of these similarities we concluded that the wavy structure belongs to band system II of Kr_2.

2. By using krypton mixed with helium or neon in the ratio 1:10-30, band system II was almost completely eliminated from the spectrum whereas system I remained strong. In the case of Ar_2, intensity of the second continuum varied in parallel to that of band system II; for example, when the band system disappeared completely, the second continuum also vanished. This relation does not hold in Kr_2 as strictly as in Ar_2, although the second continuum greatly weakened, it was still observable when band system II had disappeared. The observed evidence, however, still indicates, again as in Ar_2, that the second continuum belongs to band system II and both of these are the product of the electronic transition $5s\ ^1\Sigma_u^+\ (0_u^+) \rightarrow X\ ^1\Sigma_g^+\ (0_g^+)$, the lower state being the ground state.

3. We failed to observe band system III, $5s'\ 0_u^+ \rightarrow X\ ^1\Sigma_g^+\ (0_g^+)$, in emission and instead they appeared in absorption mixed with several of structureless emission bands which have not been previously observed in absorption (see J. Chem. Phys. 59, 5160 (1973)). The emission bands could be interpreted as produced by a free-free transition proposed for the 600 Å bands of He_2 by Mies and Smith (see J. Chem. Phys. 45, 994 (1966)).

4. Five narrow but diffuse emission bands were observed at the immediate short wavelength side of the second resonance line, 1165 Å, of KrI. The observed wavelengths agree well with those of the absorption bands previously observed (see J. Chem. Phys. 29, 5160 (1973)). The origin of these is yet to be explained.

5. Ten diffuse bands, all degraded toward short wavelengths, were observed in the 1323-1363 Å region. These can be produced strongly when one torr of krypton is excited by transformer pulsed discharge. With respect to a) the mode of excitation; b) general appearance and c) location relative to those of the first resonance line of KrI and the second continuum, the observed bands are very similar to the diffuse bands of Ar_2 mentioned earlier in this report. A quick survey was carried out on the Xenon dimer and it showed about ten diffuse emission bands in the 1585-1648 Å region which are very similar to the above Kr_2 diffuse bands. Presently, we are trying to identify the origin of these bands which should be common in Ar_2, Kr_2, Xe_2 and probably Ne_2 (see Scientific Pap. I.P.C.R. 35, 447 (1939)).

E. Rare Gas - Oxide and Chalcogenide Excimers

Recently we began a study of the higher excited states of excimers such as ArO, KrO and XeS. Although the visible bands

of these molecules have recently received considerable attention, little is known of their higher states, particularly those originating from the first excited state of the rare gas coupled to ground state oxygen or sulfur atoms. We have recently developed an efficient excitation scheme for these states involving an electrodless, radio frequency discharge in the 1-10 megahertz region. Preliminary spectra from Xenon doped with O_2 reveal a new uv band near 2350 Å in addition to the well known "green bands" and the 3000 Å continuum. The 2350 Å band appears to be correlated with the states deriving from $Xe^* + O(^3P)$. We are planning a systematic study of this band at high resolution in NeO, ArO, KrO, XeO and XeS.

Publications

1. The Vacuum uv Absorption Spectrum of O_2 from its Metastable States b $^1\Sigma_g^+$ and a $^1\Delta_g$. D.H. Katayama, S. Ogawa, M. Ogawa and Y. Tanaka, J. Chem. Phys. 67, 2132 (1977).

2. Vacuum Ultraviolet Absorption Spectra of Binary Rare Gas Mixture and the Properties of Heteronuclear Rare Gas Van der Waals Molecules. D.E. Freeman, K. Yoshino and Y. Tanaka, scheduled to appear in the November 1, 1977 issue of J. Chem. Phys.

Papers in Preparation

1. Emission Spectra of Rare Gas Dimers in the VUV: I Ar_2. To be submitted to J. Chem. Phys.

Scientific Personnel Involved in the Research:

W.C. Walker	Professor of Physics Principal Investigator
Y. Tanaka	Research Associate VI Co-Principal Investigator
Waldo Spates	Graduate student in Chemistry - UCSB Research Assistant